

Application of chemical mass balance to upstream/downstream river monitoring data

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Abstract

The river Kali in western Uttar Pradesh (India) has been heavily influenced by the discharge of untreated municipal, agricultural, and industrial effluents. In the main channel of the river, the metal contamination was found to be three to four times the background level. The concentration of iron, zinc, and copper was 0.41, 0.04, and 0.015 mg l⁻¹, respectively, in the upstream section during October. The same were 0.56, 0.07, and 0.016 mg l⁻¹, during December.

Comparisons between upstream and downstream monitoring sites reveal changes in the concentration and/or load to the river and can be used to discriminate between point and non-point sources of pollution for these elements in the river. The resulting differential loadings, if adjusted for uncharacterized non-point contribution to the load, may represent the total point source load to the river minus any losses due to volatilization, settling, and/or degradation. Mass balance calculations conducted for iron, zinc, and copper indicated that additional inputs are needed to account for the observed differences in load along the river. The sources may include non-point sources of pollution due to agricultural activities, sediment remobilization or entrainment, groundwater intrusion or from a combination of these sources. The difference may also be attributed to some point sources of pollution which could not be identified in the course of investigations.

1. Introduction

Trace quantities of heavy metals exert a positive or negative influence on plant, animal, and human life. These elements, contrary to most pollutants, are not biodegradable and undergo a global eco-biological cycle in which natural waters are the main pathways. Kaplan et al. (1987) studied the distribution of trace heavy metals along the treatment path of domestic wastewater in stabilization ponds. Bradford

(1977) reported that urban stormwater runoff has long been recognized as a major source of pollutants to surface waters.

The chemical mass balance approach has been used extensively during recent years to study the in-stream reactions and sediment dynamics (Plummer and Back, 1980; Christophersen and Wright, 1981; Elder, 1985; Yuretic and Batchelder, 1988; Latimer et al., 1988). Large retention of pollutants, particularly trace elements, in stream sediments has been reported in a number of studies. Berndtsson (1990) established water budgets and chemical mass balances of some water-quality constituents for a 5-km-long reach of the river Hoje in the south of Sweden and reported that half of the transported zinc is retained within the stream sediments. Imhoff et al. (1980) studied the heavy metals in the Ruhr river and reported that about 31% of the total load of heavy metals to the Ruhr basin are retained in the stream sediments. Katz et al. (1985) established the mass balance for major constituents in precipitation and stream water and reported that dissolved solutes from precipitation input account for 12 to 19% of the total dissolved load in stream water. Paces (1985) used mass balance models to estimate elemental budgets in the Elbe river basin.

In western districts of Uttar Pradesh (India), mainly Saharanpur, Muzaffarnagar, and Meerut, large amounts of water resources are present which are used for irrigation, fishing, or to produce fish seed and fingerlings. These water resources are also utilized for the disposal of industrial wastes of more than 20 different industries (Verma et al., 1974). The main water resources of this region are river Hindon, Kali, Krishna, Ganga, and Jamuna with their respective tributaries and four canals. Verma et al. (1974, 1975) studied the characteristics and disposal problems of various industrial effluents with reference to Indian standards. They also made a detailed survey on the pollution of river Hindon in relation to fish and fisheries (Verma et al., 1980).

The river Kali in western Uttar Pradesh receives untreated municipal and industrial effluents. The chemical characteristics of this river have been reported earlier with special reference to the disposal of municipal and industrial waste (Jain, 1992).

The river system contains a myriad of point and non-point sources of pollution. Monitoring of all such sources for all parameters everywhere is not possible. Besides, these are difficult and expensive to monitor and often present unique analytical problems and are subject to analytical error. Application of the chemical mass balance approach, for measuring the changes in the concentration and/or load to the river, provides a viable alternative and is the subject of this paper. The objective of this study is to use a chemical mass balance approach to differentiate between point and non-point contributions to the river.

2. Description of the area

The Kali river, which flows in western districts of Uttar Pradesh, is a small perennial river having a basin area of about 750 km². The area under study is a part of the Indogangetic Plains, composed of Pleistocene and subrecent alluvium

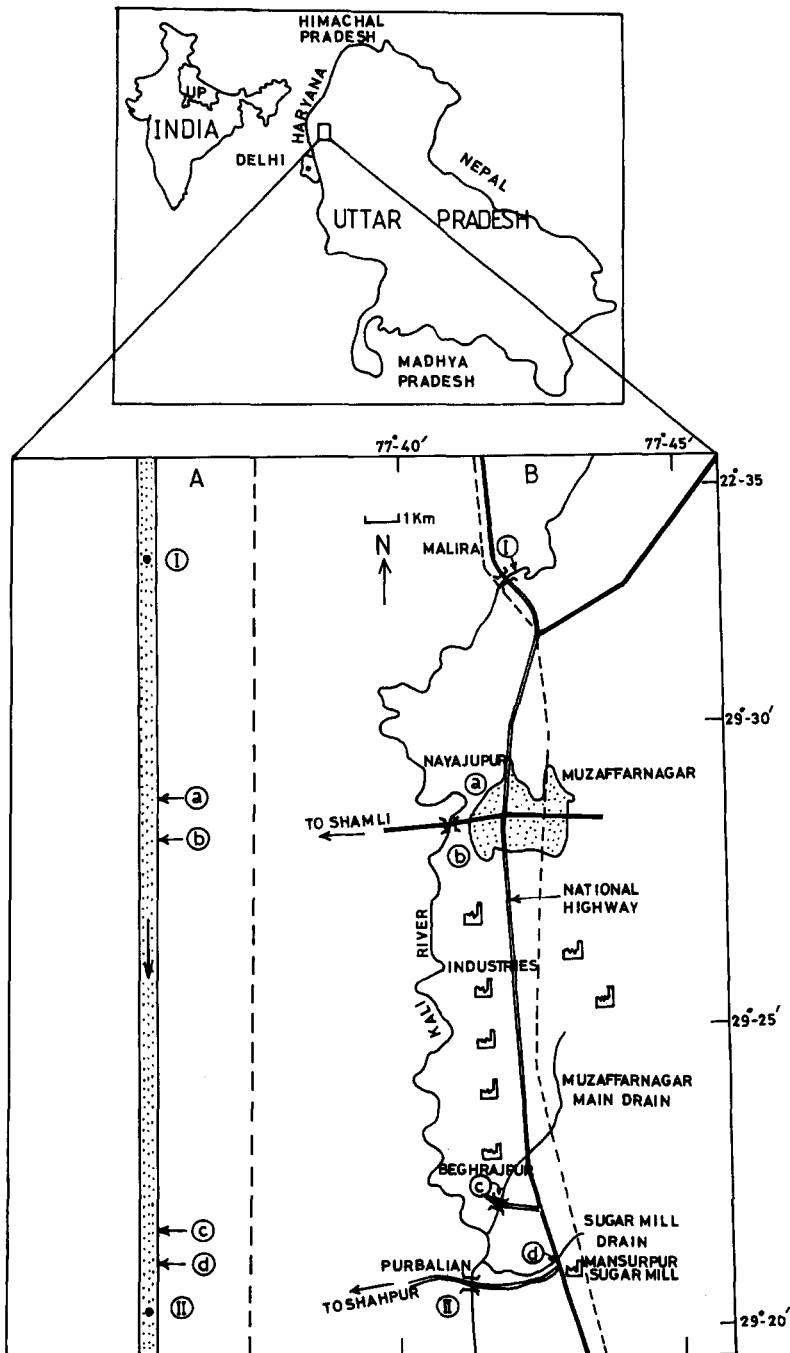


Fig. 1. River Kali – (A) Schematic representation of the system; (B) General plan of sampling locations. For details of sampling stations see Section 3.

and lies between latitude $29^{\circ}33' \text{ N}$ to $29^{\circ}21'30'' \text{ N}$ and longitude $77^{\circ}43' \text{ E}$ to $77^{\circ}39'15'' \text{ E}$ in the Muzaffarnagar district of Uttar Pradesh (Fig. 1).

The area has a moderate subtropic monsoonal climate. The average annual rainfall in the area is about 1000 mm, which is mainly received during the monsoon period. The major land use is agriculture and there is no effective forest cover. The soils of the area are loam to silty loam and are normally free from carbonates.

The river basin contains towns and villages surrounded by agricultural areas. The quantity and quality of the river water is affected by the discharge from municipal and industrial areas of Muzaffarnagar city as well as runoff from agricultural areas.

3. Sources of pollution and sampling stations

The river Kali is a typical water course for municipal and industrial effluents; all those who have access to the river use it for bathing, laundry, and even for defecating. The main sources which create pollution in river Kali include, municipal waste of Muzaffarnagar city, waste from a variety of industries (such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper, and laundries), the Mansurpur sugar mill and distillery waste. The composite waste from a variety of industries is transferred through Muzaffarnagar's main drain into the river.

The major portion of the municipal wastewater of Muzaffarnagar city flows through a system of open drains and is discharged into the river at two points. One portion of the waste having an average discharge of about $0.3 \text{ m}^3 \text{ s}^{-1}$ is discharged into the river near the village of Nayajupura while another portion of the waste having almost the same flow is discharged downstream of the bridge over the Muzaffarnagar–Shamli road. At both points, numerous people and domestic animals (cows and buffalos) bathe, and clothes washing is common just upstream of the outfalls of the municipal waste. From the point of view of river pollution and the deterioration of water quality in the bathing areas, the discharge from these drains is most critical.

A general plan of the sampling stations with respect to different outfalls of municipal and industrial effluents in river Kali is shown in Fig. 1. In all, six stations were selected for sampling – four from the outfalls of waste effluents and one each from upstream and downstream sections of the total stretch under study.

Sampling stations selected in the present study stretched over 25 km. Sampling Stations I and II are situated in the upstream and downstream sections of the stretch under study, while the other four stations, a to d, are located in the waste outfalls/drains in the river. Each station can be characterized as follows:

Station I (Malira bridge), is located in the relatively unpolluted river water zone near the village of Malira and upstream of the discharge of municipal and industrial wastes into the river. At this point the banks are high with sandy soils.

Station a, is located in the wastewater outfall near the village of Nayajupura where a part of the municipal waste of Muzaffarnagar city is discharged into the river.

Station b, is located in the municipal wastewater outfall, downstream of the bridge over the Muzaffarnagar–Shamli road.

Station c, is located in the main Muzaffarnagar drain, downstream of the bridge near the village of Begharazpur, through which the mixed waste from a variety of industries and municipal areas is discharged into the river.

Station d, is located in the sugar mill drain near Mansurpur village on the National Highway.

Station II (Mansurpur bridge), is situated near the village of Pur Balian on the Mansurpur–Shahpur road about 4 km from Mansurpur, after the outfall of sugar mill waste. The colour of the water is black and the soil is sandy mixed with organic material.

4. Methodology

4.1. Sampling and preservation

River water samples from upstream and downstream sections (Station I and II) were collected from three points (1/3, 1/2, and 2/3 width of the river) along the transect on a weekly basis using a Hydro-Bios standard water sampler during the post-monsoon period in October and December 1993. The variation in climatic conditions during the period of sampling is given in Table 1. The effluent samples from the four outfalls (Stations a, b, c, and d) were collected on a weekly basis from the middle of the drains. All samples were collected from the upper 50 cm of the water surface, filtered through a Whatman 0.45- μm pore diameter membrane filter and stored in polyethylene bottles fitted with screw caps. All containers used for collection of samples were soaked in nitric acid and rinsed with deionized water prior to use. The samples were then preserved by acidifying with concentrated ultra pure nitric acid to $\text{pH} < 2$ and stored at 4°C in polyethylene bottles. These samples were then combined to yield flow-weighted monthly composite samples prior to determination of trace elements. The discharge at all the six sampling stations was also determined during each visit using a Seba current meter by the area-discharge method.

4.2. Materials and reagents

All glassware was thoroughly cleaned by soaking in detergent followed by soaking in nitric acid for 24 h and finally rinsed with deionized water several times. All

Table 1
Variation in climatic conditions during the period of sample collection

Month	Temperature ($^\circ\text{C}$)		Relative humidity (%)	Rainfall (mm)
	Max.	Min.		
October	29.0–33.5	11.4–22.2	52–84	0.0
December	20.0–27.0	4.5–11.5	66–90	0.0

chemicals used were of ultra pure quality. Stock solutions of 1000 mg l^{-1} were prepared as follows:

Fe stock solution was prepared by dissolving 1.0 g iron wire in 50 ml of (1 + 1) HNO_3 and diluting to 1 l with deionized water.

Zn stock solution was prepared by dissolving 1.0 g zinc metal in a minimum volume of (1 + 1) HCl and diluting to 1 l with 1% (v/v) HCl.

Cu stock solution was prepared by dissolving 1.0 g copper metal in a minimum volume of (1 + 1) HNO_3 and diluting to 1 l with 1% (v/v) HNO_3 .

4.3. Sample analysis

Trace elements (Fe, Zn, and Cu) were determined by flame atomic absorption spectrometry using a Perkin–Elmer Atomic Absorption Spectrometer (Model 3110). Consequently, the results represent filterable (dissolved) metals. The detection limits for the three metal ions studied are 0.004, 0.002, and 0.002 mg l^{-1} for iron, zinc, and copper, respectively. Average value of five replicates was taken for each determination. Operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determination. Quantification of metals was based upon calibration curves of standard solutions of metals. These calibration curves were determined several times during the period of analysis.

5. Results and discussion

Table 2 contains the upstream/downstream data for the three metals studied; iron, zinc, and copper. The increase in flow between Stations I and II (upstream and downstream section of the stretch under study) was caused by the outfalls of municipal waste at Muzaffarnagar city, combined industrial waste through Muzaffarnagar main drain and Mansurpur sugar mill and distillery waste, in addition to normal baseflow.

Table 2
Upstream/downstream data for trace elements for river Kali

Element	Downstream			Upstream			Diff. load (kg day ⁻¹)
	Flow (m ³ s ⁻¹)	Conc. (mg l ⁻¹)	Load (kg day ⁻¹)	Flow (m ³ s ⁻¹)	Conc. (mg l ⁻¹)	Load (kg day ⁻¹)	
<i>October 1993</i>							
Fe	7.29	1.33	838	5.66	0.41	201	637
Zn	7.29	0.12	76	5.66	0.04	20	56
Cu	7.29	0.047	30	5.66	0.015	7	23
<i>December 1993</i>							
Fe	6.74	1.70	990	5.10	0.56	247	743
Zn	6.74	0.13	76	5.10	0.07	31	45
Cu	6.74	0.051	30	5.10	0.016	7	23

5.1. Trace elements in Kali river

The metal contamination in the downstream section was found to be three to four times greater than the upstream section. This increase was probably due to point source inputs from municipal and industrial effluents, non-point inputs from agricultural activities, and uncharacterized inputs such as groundwater intrusion, sediment–water interactions, or a combination of these sources, all of which have a cumulative impact on the river. In general, the December survey showed higher metal content in river water at both upstream and downstream sections than the October survey.

5.2. Indirect measurement of sources

Information on contributions from individual sources can be obtained by indirect measurements of the sum of sources in the receiving water using the following equation:

$$Q_D C_D - Q_U C_U = \sum_{i=1}^n L_i$$

where Q_D and Q_U are downstream and upstream flows; C_D and C_U are the downstream and upstream concentrations in the receiving water; and $\sum_{i=1}^n L_i$ is the sum of all individual loadings to the receiving water.

This simple equation is a mass budget and can be used to design a study that will result in a much more accurate estimate of $\sum_{i=1}^n L_i$ than that likely to be obtained from summing the individual loadings (due to analytical errors introduced in the analysis of a large number of individual samples).

The $\sum_{i=1}^n L_i$ term is not really the sum of loadings entering the receiving water body, but instead the net effect of the loadings plus any loss or generation within the water body. For any contaminant that undergoes significant volatilization or degradation, this approach will not give an accurate loading summation unless the time of travel between downstream and upstream is small compared with the rate constants for losses. The same is true for substances that settle from the water column.

For the October survey the differential loadings for iron, zinc, and copper were found to be 637, 56, and 23 kg day⁻¹, respectively, while for the December survey the loadings were 743, 45, and 23 kg day⁻¹ (Table 2). The upstream/downstream comparison shows significant similarities for the two surveys indicating that results may be free from seasonality. This approach may be well utilized for measuring the changes in the differential concentration and/or load to the river from year to year.

5.3. Mass balance to upstream/downstream water quality data

One of the most important aspects of water quality engineering is the determination of the input mass loading, that is, the total mass of a material discharged per unit time into a specific body of water. For defined sources with continuous flow, the input load

is given by the equation:

$$L(t) = Q(t)C(t)$$

where $C(t)$ is the concentration of the input ($M l^{-3}$), $Q(t)$ is the input flow ($l^3 T^{-1}$) and $L(t)$ is the mass rate (load) of input ($M T^{-1}$ (kilogram per second)), all quantities occurring simultaneously at given time t . In metric units, the concentration and flow are often expressed in $mg l^{-1}$ and $m^3 s^{-1}$, respectively.

The basic idea in describing the discharge of material into a river is to write a mass balance equation for various reaches of the river. For understanding the relationship between the water quality and the sources of natural and man-made pollution, the mass balance for certain water constituents is of great help. This is done by determining the load of selected substances, i.e. the weight of the substance transported through a cross-section of the river bed s^{-1} .

Table 3 contains loadings of trace elements for the major outfalls that enter river Kali in October and December 1993. For the October survey, the estimated differential loadings for iron, zinc, and copper (Table 2) compare favourably well with respect to point source loadings of 392, 32, and 15 $kg day^{-1}$ (Table 3) for iron, zinc, and copper, respectively, considering that the latter does not take into account contribution from uncharacterized non-point sources of pollution. Therefore, the difference of 245, 24, and 8 $kg day^{-1}$ in iron, zinc, and copper loadings may be attributed to the contribution of non-point sources of pollution due to agricultural activities, groundwater intrusion and/or sediment–water interactions. However, more data are needed to confirm this observation. By far the largest contribution of iron and zinc is the industrial drain which carries effluent from a variety of industries.

For the December survey, the estimated differential loadings for iron, zinc, and copper (Table 2) also compare favourably with point source loadings of 497, 35, and

Table 3
Point source loadings of trace elements to river Kali

Point source	Flow (m ³ s ⁻¹)	Conc. (mg l ⁻¹)			Load (kg day ⁻¹)		
		Fe	Zn	Cu	Fe	Zn	Cu
<i>October 1993</i>							
a	0.33	1.41	0.34	0.212	40	10	6
b	0.35	1.12	0.27	0.131	34	8	4
c	0.46	7.19	0.30	0.072	286	12	3
d	0.12	3.12	0.16	0.212	32	2	2
Total	1.26				392	32	15
<i>December 1993</i>							
a	0.30	1.61	0.37	0.216	42	10	6
b	0.34	1.49	0.28	0.133	44	8	4
c	0.46	7.98	0.27	0.014	317	11	3
d	0.23	4.74	0.28	0.232	94	6	5
Total	1.33				497	35	18

Table 4
Percentage estimate of point vs. non-point contribution

Element	Percentage estimate	
	Point sources	Non-point sources
<i>October 1993</i>		
Fe	61.5	38.5
Zn	57.1	42.9
Cu	65.2	34.8
<i>December 1993</i>		
Fe	66.9	33.1
Zn	77.8	22.2
Cu	78.3	21.7

18 kg day⁻¹ (Table 3) for iron, zinc, and copper, respectively. The difference of 246, 10, and 5 kg day⁻¹ in iron, zinc, and copper loadings may again be attributed due to the contribution of uncharacterized non-point sources of pollution. Again the largest contribution of iron and zinc was observed from the industrial drain. The percentage estimate of point vs. non-point contributions are given in Table 4. As is evident from Table 4, the point source contributions are more in December as compared with October. This was mainly due to the larger contribution from the sugar mill, which was in full swing in December.

The mass balance for iron, zinc, and copper was thus established and results are presented in Table 5. These indicate that additional inputs, above those point sources

Table 5
Loadings and mass balance calculations for trace elements

Station	Flow (m ³ s ⁻¹)	Conc. (mg l ⁻¹)			Load (kg day ⁻¹)		
		Fe	Zn	Cu	Fe	Zn	Cu
<i>October 1993</i>							
I	5.66	0.41	0.04	0.015	201	20	7
a	0.33	1.41	0.34	0.212	40	10	6
b	0.35	1.12	0.27	0.131	34	8	4
c	0.46	7.19	0.30	0.072	286	12	3
d	0.12	3.12	0.16	0.212	32	2	2
I+ (a to d)	6.92				593	52	22
II	7.29	1.33	0.12	0.047	838	76	30
<i>December 1993</i>							
I	5.10	0.56	0.07	0.016	247	31	7
a	0.30	1.61	0.37	0.216	42	10	6
b	0.34	1.49	0.28	0.133	44	8	4
c	0.46	7.98	0.27	0.074	317	11	3
d	0.23	4.74	0.28	0.232	94	6	5
I+ (a to d)	6.43				744	66	25
II	6.74	1.70	0.13	0.051	990	76	30

evaluated, are needed to account for the observed differences in load along the river. The sources may include non-point sources of pollution due to agricultural activities, remobilization from or entrainment of contaminated bottom sediments, groundwater intrusion or from a combination of these sources. The difference may also be attributed due to some point sources of pollution which could not be identified during the course of the investigations.

6. Conclusions

From the study conducted in river Kali, it can be concluded that the river is subjected to a varying degree of metal contamination due to numerous outfalls of untreated municipal and industrial wastes of the region. The discharge of municipal and industrial wastes into the river at regular intervals do not allow any self purification to occur.

The paper presents an approach to differentiate between point and non-point sources of pollution using upstream/downstream river water quality data. This approach is useful to estimate the load to the river and detect changes in the water quality characteristics within the river system. The levels of trace elements in the downstream section indicate that additional inputs account for the observed differences in load along the river. Indirect monitoring of point sources using upstream/downstream sampling locations provides a better alternative over other conventional techniques. An additional advantage of this approach is the substantial reduction in cost involved in the analysis of a large number of individual samples.

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